1994

NASA/ASEE SUMMER FACULTY FELLOWSHIP PROGRAM

MARSHALL SPACE FLIGHT CENTER
THE UNIVERSITY OF ALABAMA

GROWTH OF THIN FILMS OF DICYANOVINYLANISOLE ON QUARTZ AND TEFLON-COATED QUARTZ BY PHYSICAL VAPOR TRANSPORT

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INTRODUCTION

For a number of years now, nonlinear optics has been a field receiving intense research effort. This activity has been spurred by the tantalizing potential for developing optical equivalents of wires (wave guides), switches and gates (threshold sensitive devices). In theory, at least, these may be formulated and interconnected to produce all-optical computers, holographic pattern recognition devices and electro-optical modulators and multiplexers. Such optical devices can carry much more information and operate at the speed of light.

Early work in nonlinear optical devices centered around inorganic crystalline materials such as quartz, potassium dihydrogen phosphate and lithium niobate and more recently of materials such as $KTiOPO_3$, BaB_2O_4, and LiB_3O_5. Organic materials are now receiving attention due to the discovery of organic crystals with nonlinearities which are orders of magnitude greater than that of the best inorganic crystals.

Organic compounds offer the possibility of molecular engineering in order to optimize the nonlinearity and minimize damage due to the high-power laser used in such devices. Recently dicyanovinylanisole (DIVA), {[2-methoxyphenyl]methylenepropanedinitrile} has been shown to have a second order nonlinearity 40 times that of α-quartz[1].

Organic crystalline materials have disadvantages for fabrication into optical devices because they often lack the mechanical stability required for grinding and polishing into high-quality optical surfaces. Thin crystalline films may offer the advantages of organic crystals without the need for further mechanical fabrication.

Orientational order of the organic molecules is important to the production of nonlinear optical signals from bulk samples[2]. Many techniques have been used to bring organic molecules into bulk orientational order. These include: Langmuir-Blodgett films[3,4,5], stretched polymeric films[6], electric field (corona discharge) poling[7,8,9,10], growth on oriented Teflon[11] and vapor deposition[12,13,14,15].

Debe *et.al.* [16,17,18] have shown that a high degree of orientational order exists for thin films of phthalocyanine grown by physical vapor transport in microgravity. The microgravity environment eliminates convective flow and was critical to the formation of highly ordered dense continuous films in these samples.

This work seeks to discover the parameters necessary for the production of thin continuous films of high optical quality in Earth gravity. These parameters must be known before the experiment can be planned for growing DIVA in a microgravity environment. The microgravity grown films are expected to be denser and of better optical quality than the unit gravity films as was observed in the phthalocyanine films.

EXPERIMENTAL

DIVA was prepared by reaction of o-methoxybenzaldehyde with malononitrile in a single-step reaction. The resulting compound was separated from unreacted starting material and purified by fractional crystallization from acetone solution(19). The molecular structure is shown in Figure 1 below.
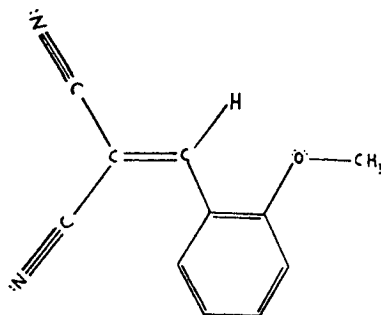

Figure 1 Molecular Structure of DIVA

Two features of the molecular structure of DIVA are important to its high nonlinear optical properties. These are extensive π-electron delocallization and a planar configuration which preserves the overlap of orbitals necessary for the delocallization. The planar configuration is the result of hydrogen bonding between the vinyl hydrogen and the oxygen atom on the ortho position of the aromatic ring. DIVA crystallizes in the $P2_1$ noncentrosymmetric space group of the monoclinic crystallographic system(1).

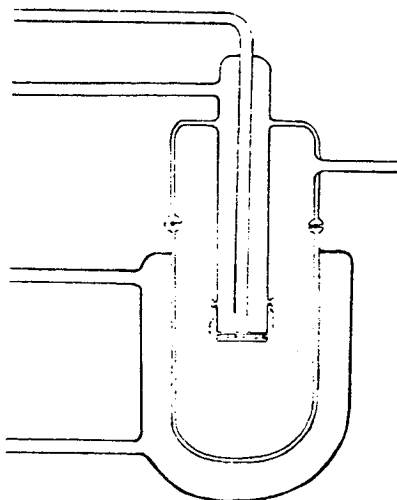The physical vapor transport apparatus is shown in Figure 2.

Figure 2 Physical Vapor Transport Apparatus

The optimum conditions for growth of good quality films were: a substrate temperature between 0 and 5°C, a sample temperature between 20 and 45°C, a cell pressure between 5 and 30 millitorr and a deposition time between 1 and 3 minutes.

The quality of the films was examined under polarized light using a Zeiss Ultraphot II optical microscope. The magnification was approximately 100X. Films were viewed in both reflectance and transmittance. Transmittance was used to observe the extinction of single-crystalline areas as the polarization of the analyzer was changed. This allows an estimate of the size of single crystalline areas within the film. All photographs (used in later figures) were taken in reflectance mode because more surface details were visible making it easier to judge the quality of the resulting film.

Film Stability

When initially deposited, the films appear amorphous, being composed of randomly oriented small specks with no indication of the linear edges and fixed angles characteristic of crystalline materials. (See Figure 3--Left Side.) However, within a matter of minutes the smaller particles begin to disappear and small crystals begin to form. Typically, within 24 hours, most of the evidence of the amorphous film will have vanished and well-defined crystal plates will have formed. (See Figure 3--Right Side.)

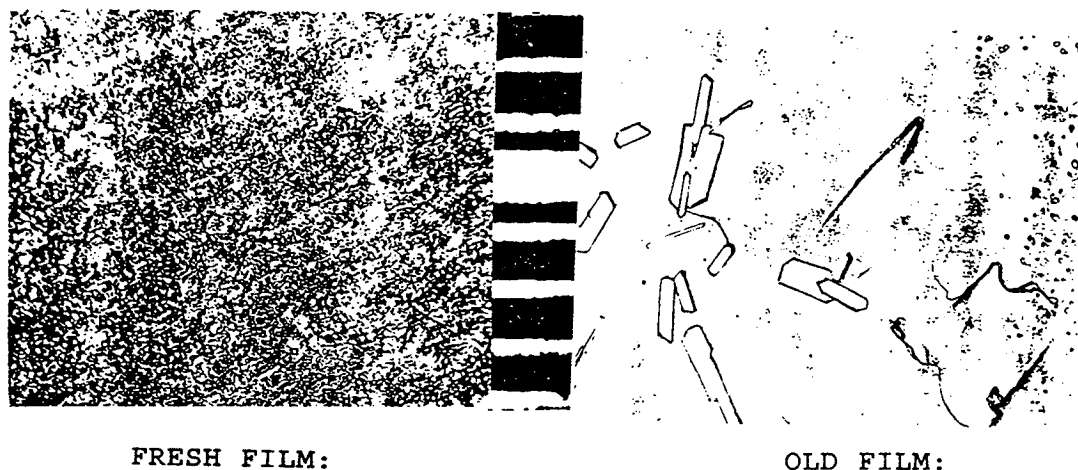FRESH FILM: OLD FILM:

Figure 3 Film Stability
The spacing between the small white lines in the center of the figure is 0.1 mm.

This behavior is observed for both Teflon coated and uncoated fused quartz substrates. At substrate temperatures greater than $10^{\circ}C$, and pressures greater than 150 millitorr, crystalline material is formed initially and the amorphous film is not observed.

At temperatures below $5^{\circ}C$, the initial film is composed of randomly positioned super-cooled liquid droplets which crystallize within a matter of minutes. During the time that crystals are forming and growing, the smallest drops disappear and larger ones in the vacinity grow even larger. This is similar to the process known as Ostwald ripening by which vapor is transported from small droplets to larger ones. The driving force for migration is the surface free energy of molecules on droplets. The surface free energy decreases as the radius of curvature increases.

Film Uniformity

While most of the film appears uniform, a small region around the edge is quite different. The edges tend to be more thickly coated than the center while the amorphous film is present. After the film has reached edquilibrium, the center appears coated with small micro crystals with their long axis lying in the plane of the film but randomly placed on the surface of the substrate. (See Figure 4--Left Side.) The edge is covered with crystalline material with no linear sides and no definite angles. Under polarized light, the edge is found to be composed of large irregularly shaped plates with the same orientation of crystallographic axes. (See Figure 4--Right Side.)

CENTER: EDGE:

Figure 4 Film Uniformity
The spacing between the small white lines in the center of the figure is 0.1 mm.

Teflon Coated Substrates

Pooley and Tabor(20) showed that thermoplastic polymers form oriented films when frictionally transferred to flat substrates. Since this early work, others have used atomic force microscopy to show that a Teflon film surface is composed of separated aligned molecules in which the individual fluorine atoms are resolved(20,21). It has also been demonstrated that these films are also effective in orienting other molecules which are deposited on them(11).

The crystalline films shown in Figure 4 were deposited on Teflon coated quartz substrates. It is obvious that voids between the micro crystals follow the drag direction on the Teflon film (vertical). It is also noted that the long axis of the micro crystals are somewhat ordered relative to this direction also. The most dominant angle is about 45°. It is intriguing that the fluorine atoms follow a helical twist angle of about 42° relative to the molecular axis.

DISCUSSION

The observations of this work can be qualitatively explained by assuming that the topography of the surface of the substrate gives rise to regions of varying attractive potential energy for DIVA molecules. The regions of lowest potential energy are probably randomly (not isotropically) ordered. Most sites are probably much farther apart than the distance between

DIVA molecules in single crystals. The DIVA molecules migrate along the surface finding the minimum energy for the entire assembly. The surrounding temperature provides the thermal energy necessary (activation energy) for moving molecules from site to site along the surface until a suitable seed crystal fragment is formed. (The migration of molecules might also occur through a supercooled liquid layer on the surface.)

The "edge effect" might arise from a temperature difference between the center and the edge of the substrate, a radial temperature gradient along the gas layer in contact with the substrate, or convective flow around the edges of the substrate.

It is found that a crystalline film similar to that observed on the edges is formed at low temperatures ($0^{\circ}C$). This would seem to indicate that the isotropic film has a low activation energy for migration. At low temperature, the amorphous film forms "droplets" of supercooled liquid. The slower migration at lower temperature produces fewer seed crystals, resulting in larger, more irregularly shaped crystal fragments which merge into each other.

RECOMMENDATIONS

All the results should be reproduced as similar studies are carried out involving other organic compounds. If these effects are common to other materials, the temperature and pressure should be referenced to the critical temperature and pressure to see if a pattern exists. The kinetics of transition between the amorphous and the crystalline forms should be studied.

Since the interest in these films is for their nonlinear optical properties, techniques for protecting the film should be investigated. Perhaps they could be coated with a polymer film or other material.

The orientation of DIVA molecules in the films would be measured using polarized infrared spectroscopy as has been done for other films (16,23,24,25). It would also be interesting to study the films formed on cleaved crystalline substrates such as quartz, KBr and NaCl .

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